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# Tentative identification of new-generation per- and polyfluoroalkyl substances in industrial products

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## PFAS in Industry and the Environment

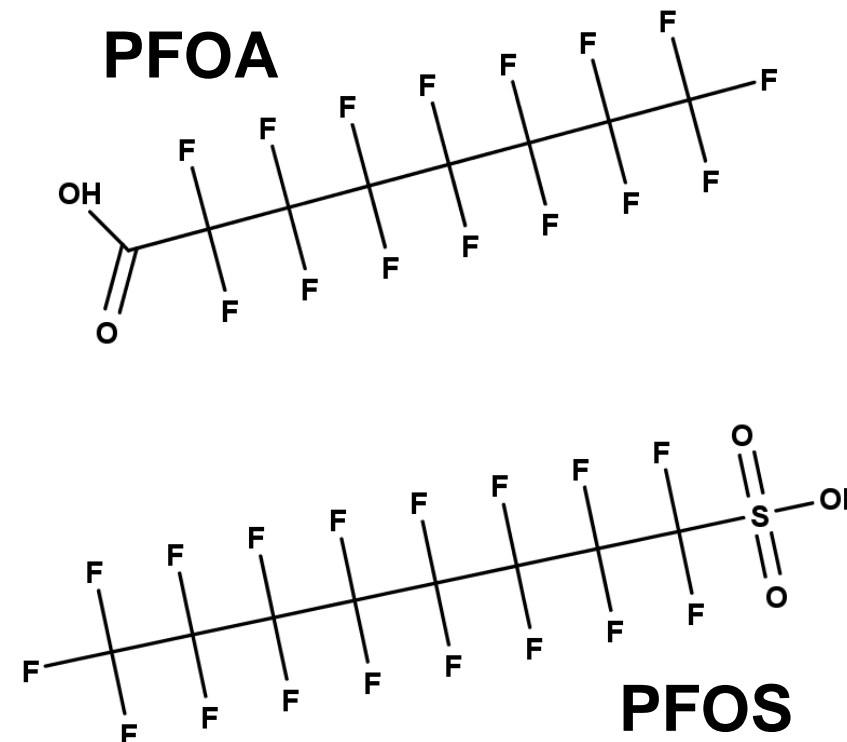
Per- and polyfluoroalkyl substances (PFAS) are contaminants of emerging concern due to their persistence in the environment and in the human body, coupled with evidence of adverse health effects linked to exposure. These compounds have become ubiquitous in industry and the environment, and identifying their composition and structure is critical for assessing environmental exposure and hazard.

### Industrial Applications of PFAS

PFAS possess desirous chemical properties, such as heat, stain, and water resistance that have led to their widespread use in consumer products and as manufacturing aids. Some of these industrial applications include:

- Aqueous film-forming foams (AFFFs)<sup>1</sup> commonly used in firefighting
- Oil-resistant coatings for paper and food packaging
- Stain-repellents and protectors for textiles
- Surfactants and reactants in the synthesis of fluoropolymers

Perfluorooctanoic Acid (PFOA) and perfluorooctane sulfonate (PFOS) have been voluntarily phased out by industries in the United States. However, these legacy compounds are still manufactured internationally. Furthermore, the development of replacement chemicals, such as GenX, is proving to be a continuously-evolving source of new PFAS in the environment.



### PFAS in the Environment

PFAS can enter the environment through industrial discharge, consumer products, and the degradation of fluorotelomer-based polymers.<sup>2</sup> A variety of these compounds have been detected in groundwater,<sup>1</sup> soil,<sup>3</sup> and surface waters,<sup>4</sup> which provide exposure routes for humans and wildlife.

## PFAS in New Hampshire

EPA ORD has been working with EPA Region 1 and New Hampshire Department of Environmental Services (NHDES) to analyze industrial and environmental samples potentially containing PFAS compounds.

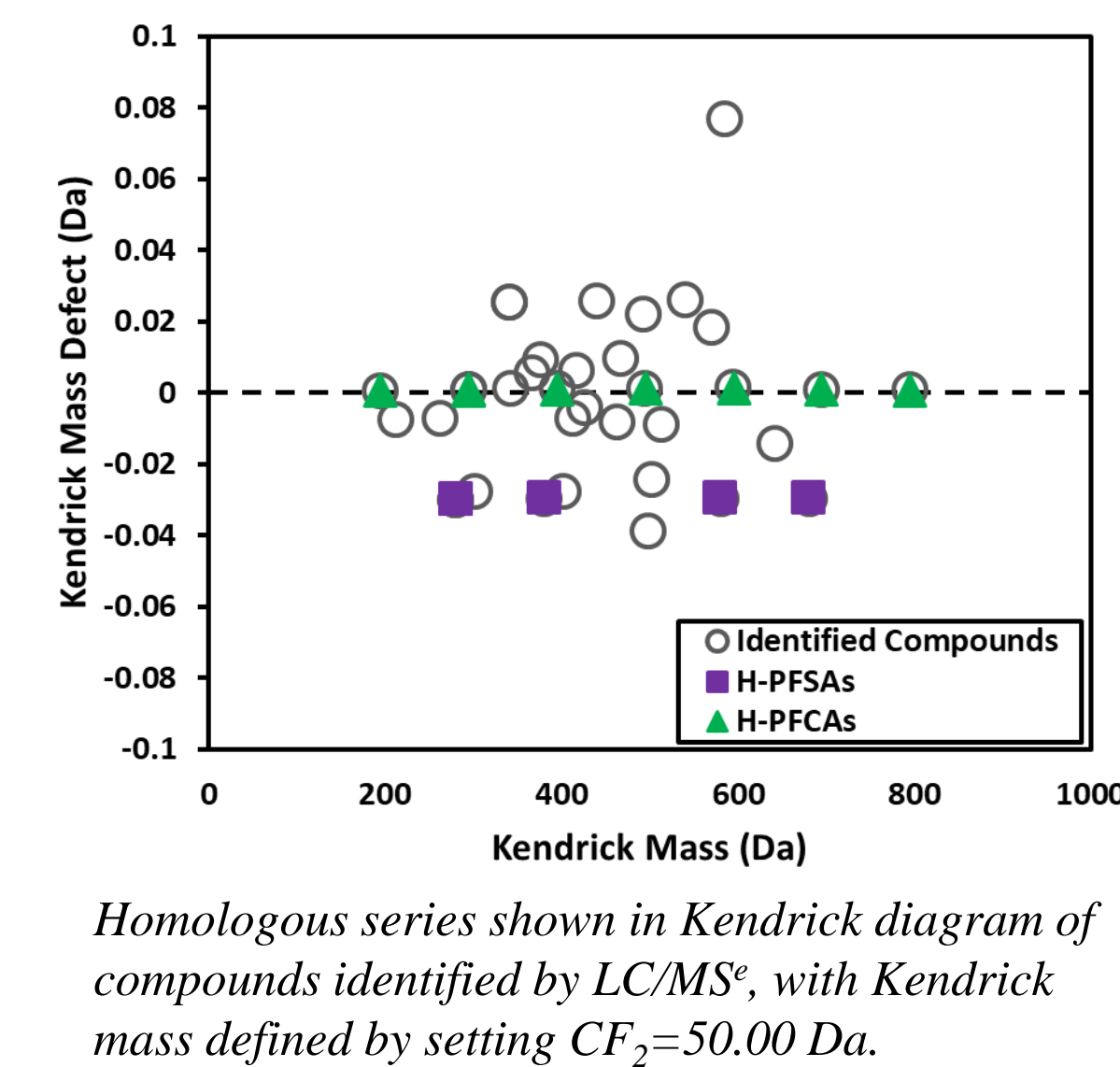
- Environmental samples were collected by NHDES staff at two NH industrial manufacturing facilities and include char samples from smokestacks and samples from surrounding soil
- Stock samples from 13 different industrial products (labeled Dispersions #1-13 for analysis) were also collected by NHDES staff
- Recently, 40 perfluorinated compounds were tentatively identified in the industrial dispersions via high-resolution liquid chromatography mass spectrometry (LC/MS) in MS<sup>e</sup> mode and conventional-resolution gas chromatography mass spectrometry (GC/MS). These compounds were included in a report to NHDES in May 2019.

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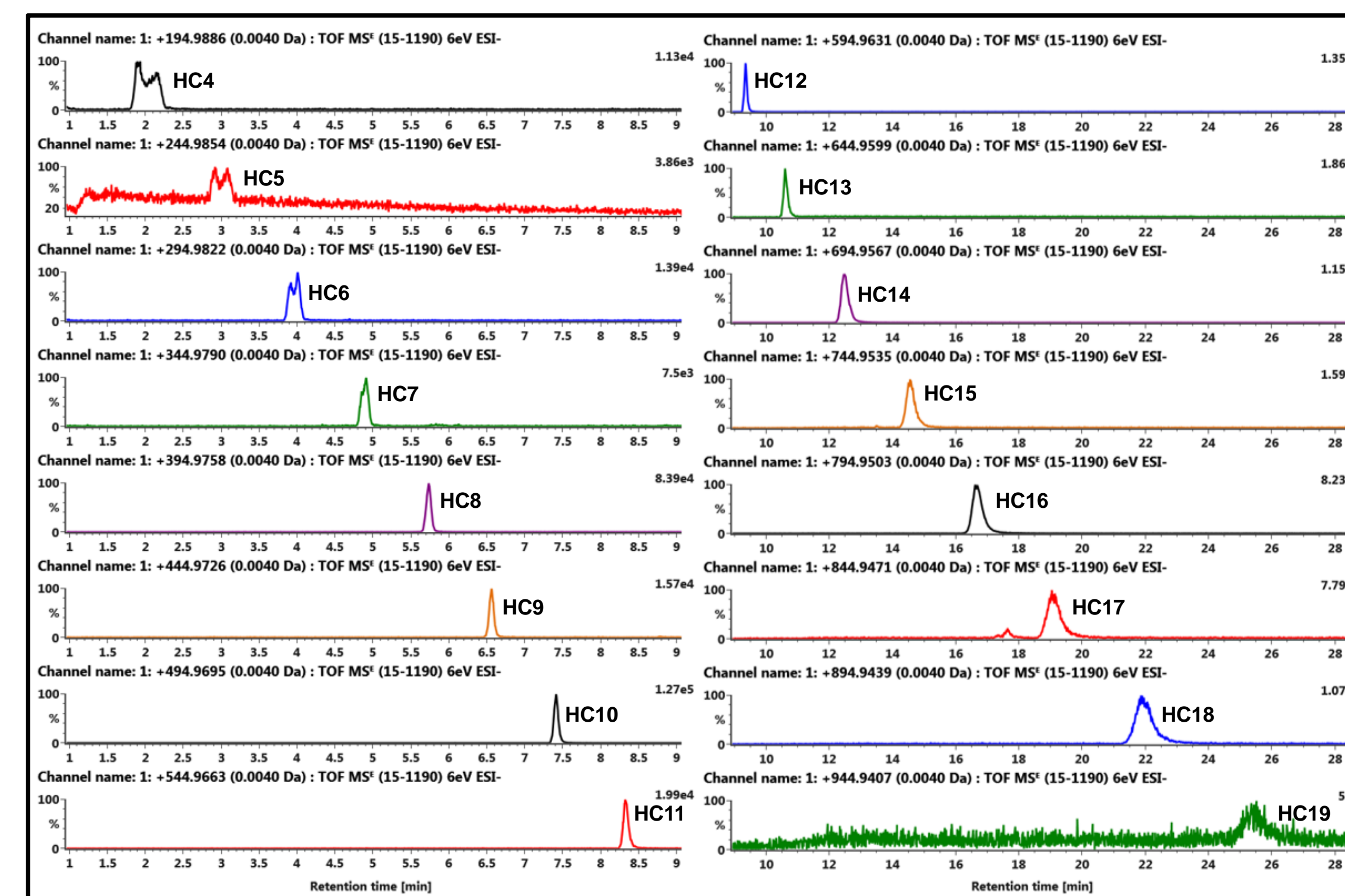
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Office of Research and Development

## Tentative Identification of H-PFCA and H-PFSA Series

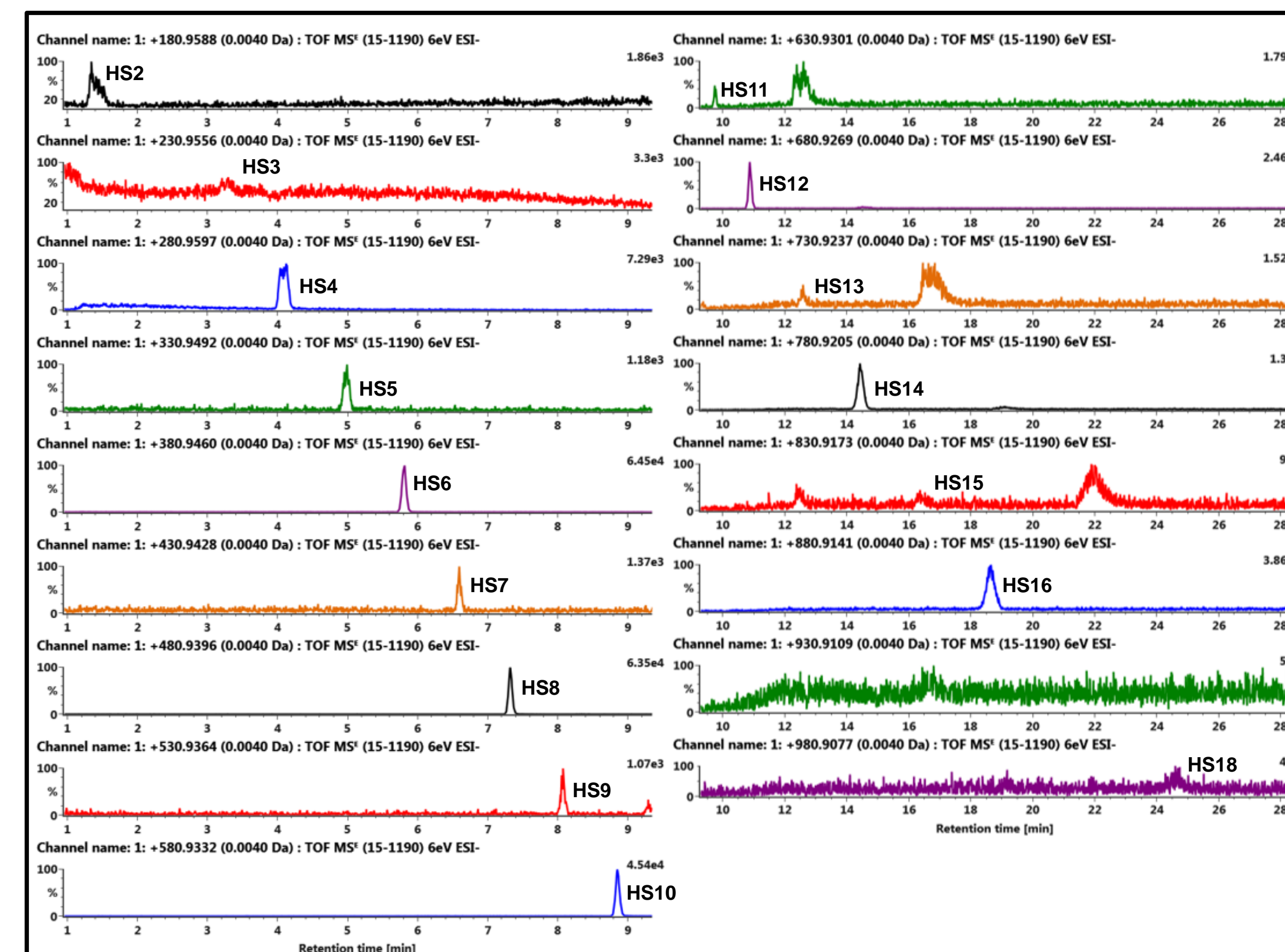
Two homologous series were detected in non-targeted analysis of environmental samples and Dispersion #3. High-resolution LC/MS in MS<sup>e</sup> mode and fragmentation patterns enabled the tentative identification of these series as hydrogenated polyfluorinated carboxylic acids (H-PFCAs) and hydrogenated polyfluorinated sulfonic acids (H-PFSAs).



Homologous series shown in Kendrick diagram of compounds identified by LC/MS<sup>e</sup>, with Kendrick mass defined by setting CF<sub>2</sub>=50.00 Da.



Extracted ion chromatograms (LC/MS in MS<sup>e</sup> mode) for H-PFCA series found in both environmental and dispersion samples. Shown here in environmental sample of char discharge from an industrial stack, diluted 10,000x in ACN/H<sub>2</sub>O.

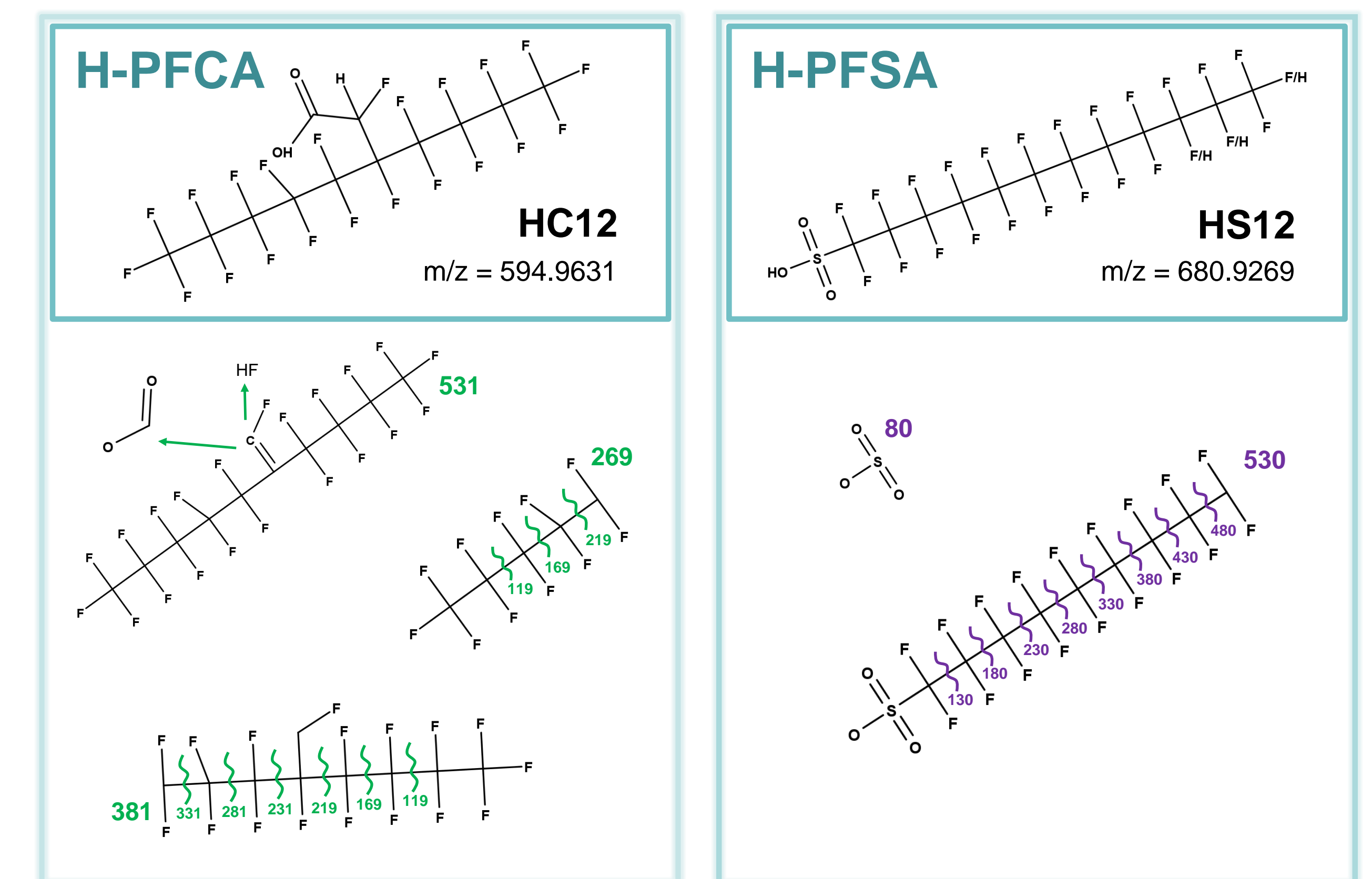


Extracted ion chromatograms (LC/MS in MS<sup>e</sup> mode) for H-PFSA series found in both environmental and dispersion samples. Shown here in environmental sample of char discharge from an industrial stack, diluted 10,000x in ACN/H<sub>2</sub>O.

## Targeted Analysis of H-PFCA and H-PFSA Series

### Structure Elucidation of H-PFCA and H-PFSA Series

In order to minimize uncertainties associated with compound coelution in MS<sup>e</sup> mode, the samples were analyzed via high-resolution LC/MS in MS/MS mode. This targeted analysis provided more confidence in precursor-fragment pairings, enabling the elucidation of hydrogen position and branching structure.

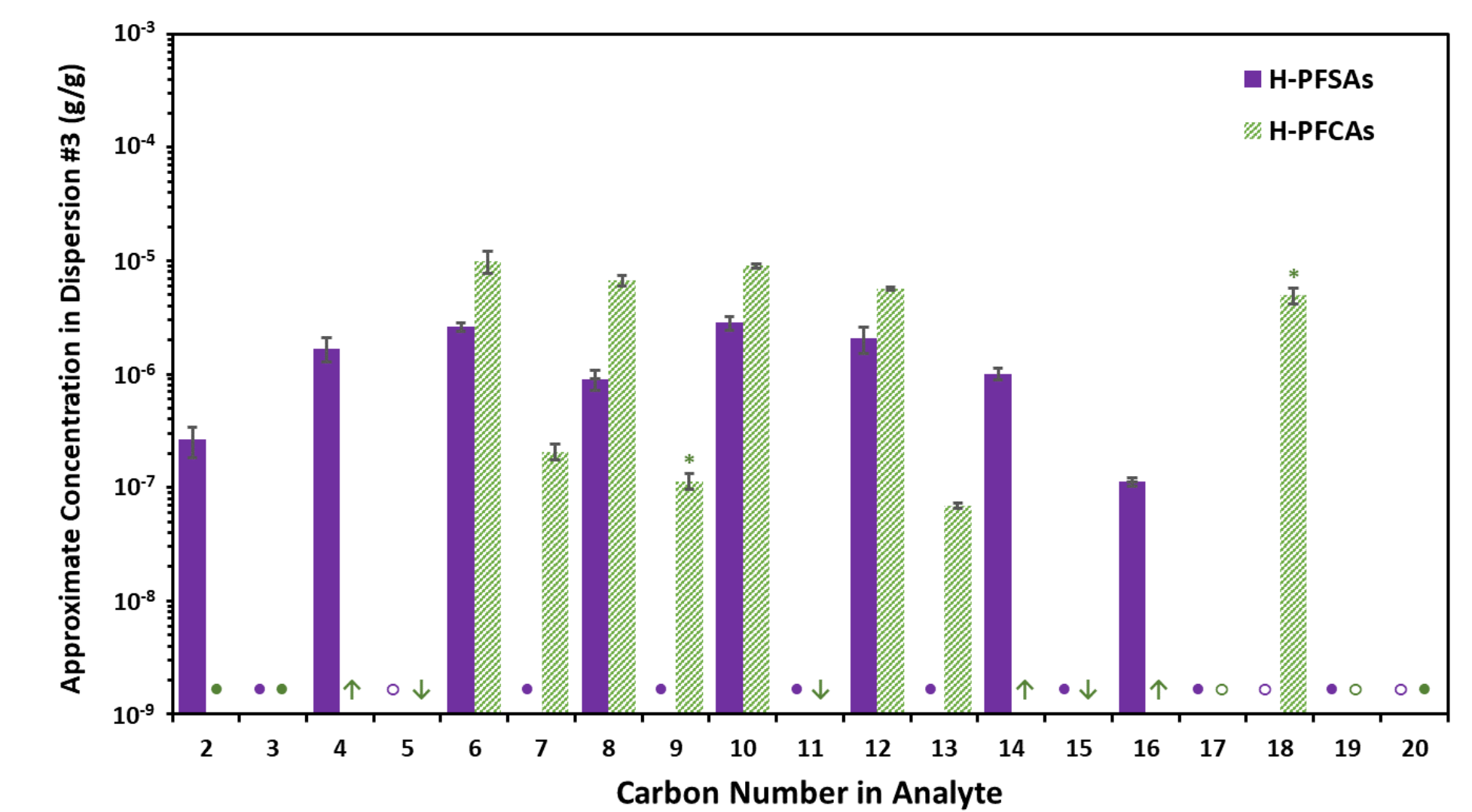


Proposed structure of HC12, indicating position of hydrogen, branching, and common fragments as inferred from high-resolution LC/MS in MS/MS mode

Proposed structure of HS12, indicating approximate position of hydrogen and common fragments as inferred from high-resolution LC/MS in MS/MS mode

### Semi-Quantitation of H-PFCA and H-PFSA Series

Conventional-resolution LC/MS/MS revealed analyte concentrations at ~ppm levels in Dispersion #3. For semi-quantitation, H-PFCAs and H-PFSAs were compared to commercially available PFCA and PFSA standards of similar molecular weight.



Order-of-magnitude semi-quantitation of H-PFSAs and H-PFCAs revealed that these compounds are present in industrial dispersion #3 at ~ppm levels. Symbols indicate: \* only 2/3 replicates within calibrated standard range; ○ Non-detect; ● Not analyzed; ↓ Detect, below calibrated standard range; ↑ Detect, above calibrated standard range.

## References

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